Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Multi-Color Emission with Orthogonal Input Triggers from a Diarylethene Pyrene-OTHO Organogelator Cocktail

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Content

A. General Information

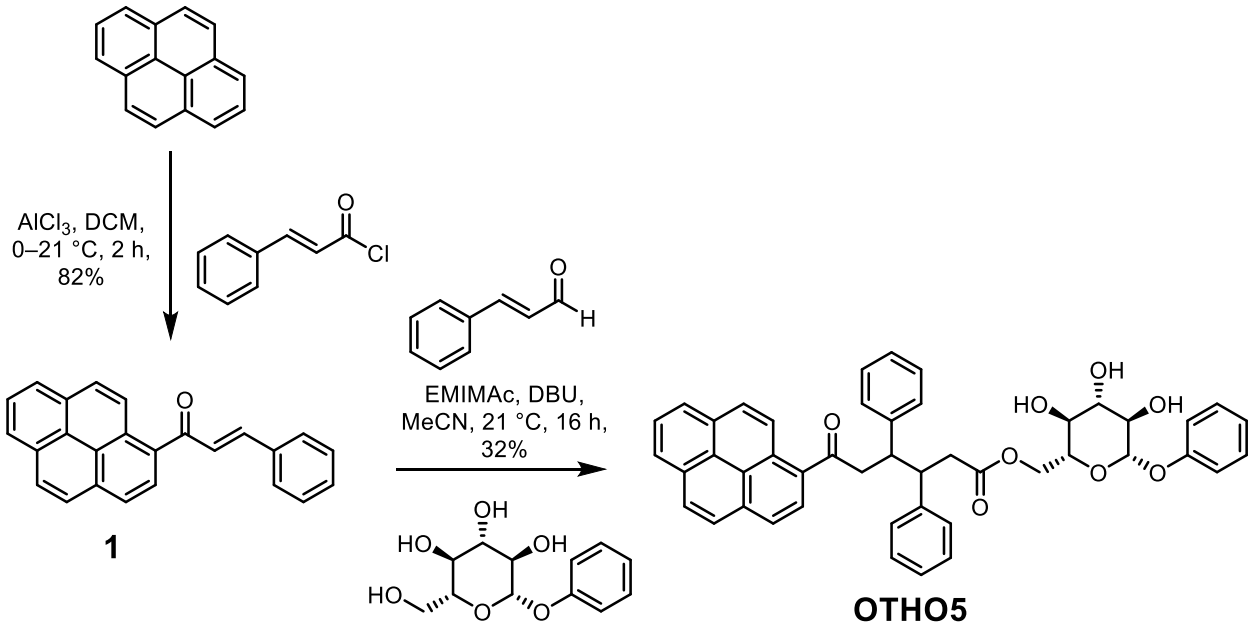
All reagents and solvents were purchased from Sigma-Aldrich and Alfa Aesar and used without any further purification. Purification of reaction products was performed by silica gel column chromatography. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra were acquired on an Agilent NMR machine at 25 °C. The chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) relative to the residual peak from solvent $CDCl_3$ and DMSO-d_6 as the internal standard; ^{1}H NMR signal at δ 7.26 ppm and ^{13}C NMR signal at δ 77.1 ppm for $CDCl_3$. ^{1}H NMR signal at δ 2.50 ppm and ^{13}C NMR signal at δ 39.5 ppm for DMSO-d_6. All coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated by s (singlet), d (doublet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublets of doublets), triplet (t), dt (doublet of triplet) and m (multiplet).

High-resolution mass spectrometry data was measured on an Agilent QTOF 6520 by the CMSI service at Chalmers University of Technology. Confocal laser scanning microscopy (CLSM) was measured on a Nikon Ti-E/A1+, using a 60X NA 1.4 DIC objective, and 405 nm excitation laser. The rheological measurements were acquired using a TA instruments DHR-3 with a sand blasted parallel plate geometry. The measurements were performed using a plate diameter of 40 mm, a gap of 400 µm, and at a temperature of 20 °C. The rheometer was equipped with a solvent trap to reduce solvent evaporation. The standard experimental parameters used a strain of 0.5%, and frequency of 6.28 rad.s^{-1}.

All the photophysical measurements were performed at 1 atm and room temperature. Ground state UV-Vis absorption spectra were recorded on a Cary 4000 UV/Vis spectrometer. Steady-state emission spectra were recorded on a SPEX Fluorolog-3 spectrofluorometer. Fluorescence lifetimes measurements were performed using time-correlated single photon counting (TCSPC) setup. The excitation light was provided by a 377 nm diode laser (LDH-P-C-375) powered by a PDL-800B pulsed diode driver (Picoquant, GmbH Germany). The emitted photons were collected at the magic angle (54.7°) with a thermoelectrically cooled microchannel plate photomultiplier tube (R3809U-50, Hamamatsu). The signal was digitalized using a multi-channel analyzer with 1024 channels (SPC-300, Edinburgh Analytical Instruments) and 10000 counts were reached in the top channel. The fluorescent lifetime decays were fitted using the program FluoFit Pro v.4 (PicoQuant GmbH, Germany) after deconvolution of the data with the instrument response function (IRF) with FWHM~40 ps. The quality of the fit was assessed by minimizing the reduced χ^2 function and by visual inspection of the weighted residuals.

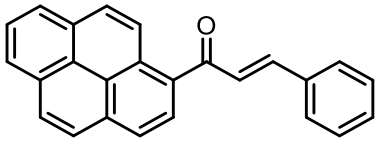
The gels were prepared by gently heating the OTHO gelator with different solvents until complete solvation in sealed 4 mL vials. Gels formed upon cooling to room temperature, while sonication aided the gel formation in some cases when using toluene/acetonitrile solvent mixtures. For OTHO5/DAE8, the samples were prepared in a dark room to avoid undesired isomerization reactions. The DAE8, OTHO5 and solvent (toluene/acetonitrile=2/1) were added into a 4 mL vial and gently heated until all the compounds dissolved. Then the hot mixture solution was transferred to a quartz cuvette. The gel was formed with an assistance of sonication for 10 minutes.

B. Synthesis of OTHO gelator



Scheme S1. Synthesis of **OTHO5**

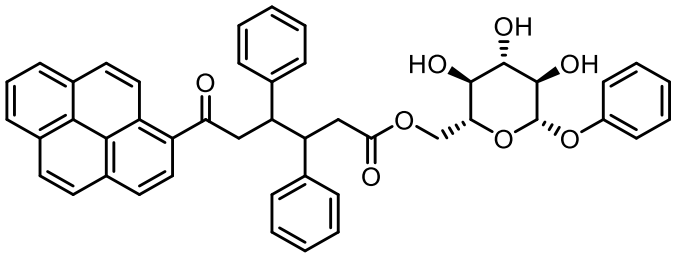
Compound 1



Pyrene (1.00 g, 4.94 mmol) was added in a 250 mL double-neck round flask and degassed three times. $AlCl_3$ (791 mg, 5.93 mmol) was added, followed by anhydrous CH_2Cl_2 (40 mL). The solution was cooled below 0 °C in an ice-bath before a solution of cinnamoyl chloride (989 mg, 5.93 mmol) in anhydrous CH_2Cl_2 (10 mL) was slowly added. After stirring for 2 hours at 21 °C, ice cold concentrated HCl (5 mL) was added. The reaction mixture was stirred for 15 min and poured onto ice. The product was then extracted with CH_2Cl_2, and then washed with water (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/heptane = 1/2) to give the desired compound **1** (1.35 g, 82%) as a yellow powder. The ^{1}H NMR spectrum matched that reported in the literature (D. Tong *et al*., *Sensors and Actuators B*, **2014**, *195*, 80–84).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.62 (d, *J* = 9.3 Hz, 1H), 8.29–8.21 (m, 4H), 8.19 (d, *J* = 8.3 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 16.0 Hz, 1H), 7.61 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.42 (dd, *J* = 4.2, 2.3 Hz, 3H).

OTHO5



Pyrene chalcone (1.00 g, 3.01 mmol), β-D-glucopyranoside (2.30 g, 9.03 mmol) and 70 mL of acetonitrile were added into a 250 mL round flask. Then, cinnamaldehyde (0.76 mL, 6.02 mmol) and EMIMAc (1.25 mL, 7.52 mmol) were added to the mixture, causing complete solvation of the sugar. DBU (0.23 mL, 1.50 mmol) was added and the solution was stirred at 21 °C for 16 hours. The reaction mixture was concentrated under vacuum to approximately 10 mL, then water (20 mL) was added. Evaporation of residual acetonitrile resulted in a fine slightly yellow precipitate that was collected by vacuum filtration, washing with water. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/methanol = 10/1) to give the desired compound (0.70 g, 32%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.20 (dd, *J* = 9.7, 7.6 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.08 (dd, *J* = 9.3, 1.1 Hz, 1H), 8.00–8.06 (m, 3H), 7.97 (d, *J* = 9.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.46–7.33 (m, 4H), 7.32–7.15 (m, 8H), 7.10–6.90 (m, 3H), 4.79 (t, *J* = 6.8 Hz, 1H), 4.38 (dd, *J* = 12.5, 3.5 Hz, 0.5H), 4.30 (dd, *J* = 12.4, 4.2 Hz, 0.5H), 3.99 (dd, *J* = 12.4, 2.3 Hz, 0.5H), 3.92 (dd, *J* = 12.4, 2.1 Hz, 0.5H), 3.69–3.35 (m, 7H), 3.31 (dt, *J* = 9.6, 2.9 Hz, 1H), 3.21 (d, *J* = 3.7 Hz, 0.5H), 3.17 (d, *J* = 3.8 Hz, 0.5H), 3.04 (t, *J* = 9.1 Hz, 0.5H), 2.70 (t, *J* = 9.0 Hz, 0.5H), 2.63–2.41 (m, 3H).
^{13}C NMR (101 MHz, DMSO-d_6, 298 K) δ 203.4, 171.2, 171.1, 157.2, 157.1, 142.3, 142.2, 132.9, 132.8, 130.6, 129.9, 129.32, 129.25, 128.7, 128.52, 128.47, 128.4, 128.33, 128.27, 127.9, 127.1, 126.8, 126.72, 126.68, 126.3, 125.9, 125.79, 125.76, 124.2, 124.1, 123.8, 123.4, 121.8, 116.2, 116.1, 100.0, 99.9, 76.28, 76.26, 73.7, 73.4, 73.08, 73.05, 70.0, 69.8, 63.5, 63.4, 47.4, 47.3, 47.14, 47.11, 46.7, 38.7, 38.5.
HR-MS (ESI) for calcd for $C_{46}H_{40}O_8$: 721.2796 ($[M+H]^+$); found 721.2796.

C. Gel formation test in different solvents

Table S1. Gelation tests in different solvents.

	OTHO5 (10 mg/mL)
toluene	G
acetonitrile	PG
ethyl acetate	G
isopropanol	P
ethanol	P
THF	S
glycerol	Sus
dichlorobenzene	G
toluene/acetonitrile = 9/1	G
toluene/acetonitrile = 3/1	G
toluene/acetonitrile = 2/1	G
toluene/acetonitrile = 1/1	S
toluene/acetonitrile = 1/2	PG

G: gel, PG: partial gel, S: solution, P: precipitate, Sus: suspension

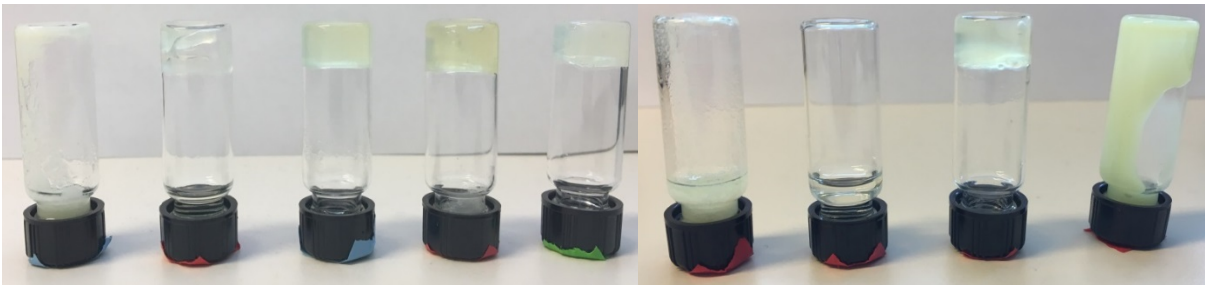


Figure S1. Gelation tests of **OTHO5** in different solvents (10 mg/mL) at room temperature. From left to right: Isopropanol; Acetonitrile; Dichlorobenzene; Toluene; Toluene/Acetonitrile = 2/1; Ethanol; THF; Ethyl Acetate; Glycerol.

D. Rheology data

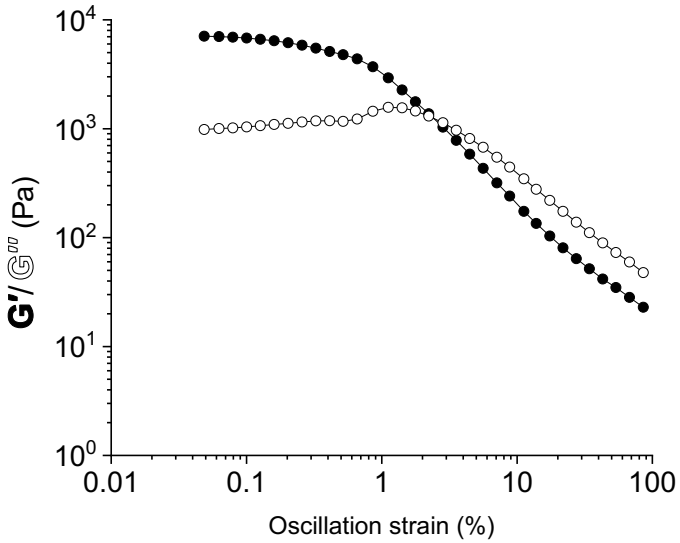


Figure S2. Strain sweep of **OTHO5** gel, 10 mg/mL in toluene, G′ = ●, G′′ = ○. Frequency = 6.28 rad. s^{-1}.

E. Confocal Microscopy

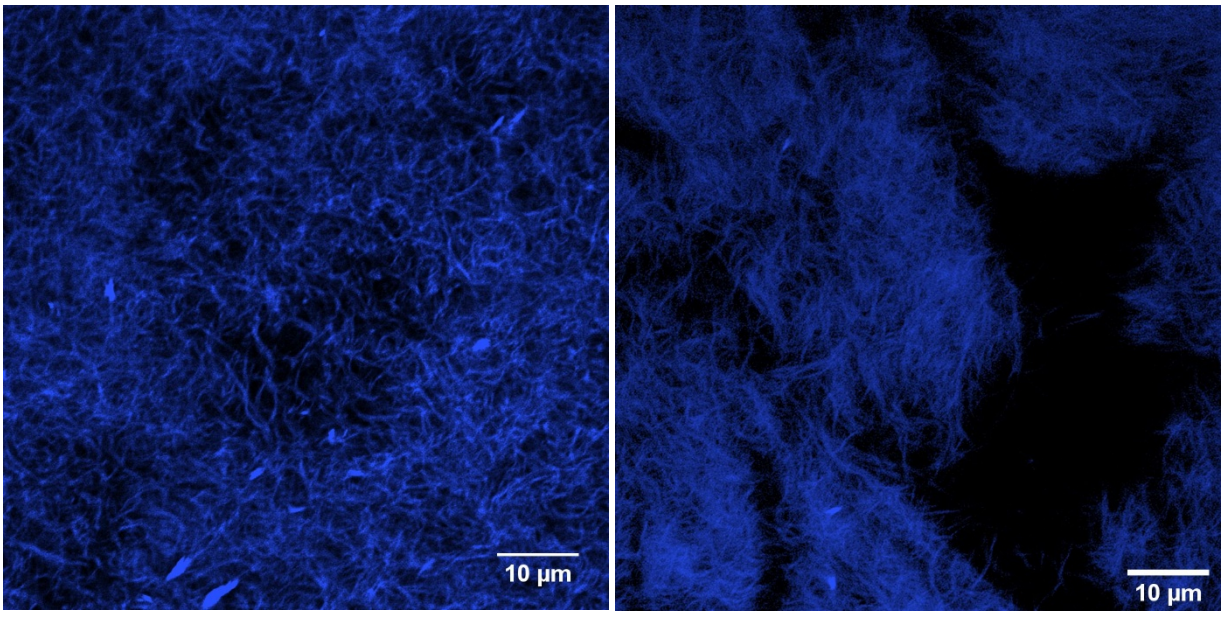


Figure S3. CLSM images of **OTHO5**, 10 mg/mL in toluene (left), and 2:1 toluene/acetonitrile (right).

F. Photophysical properties

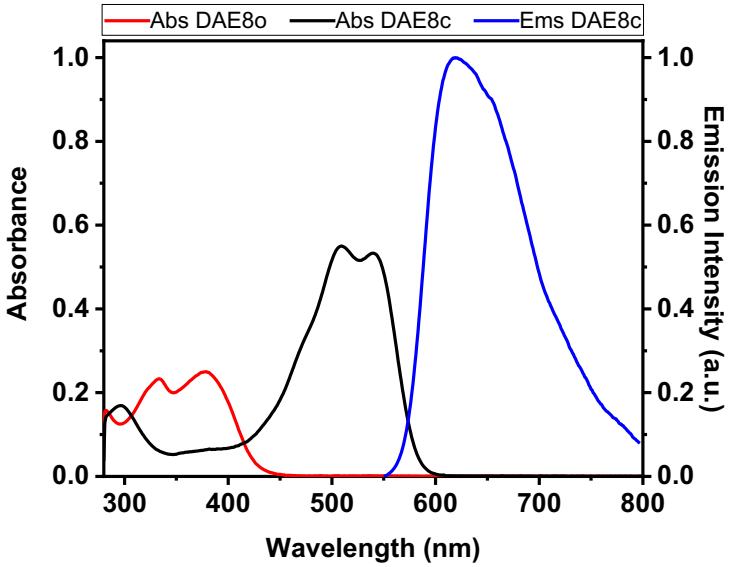
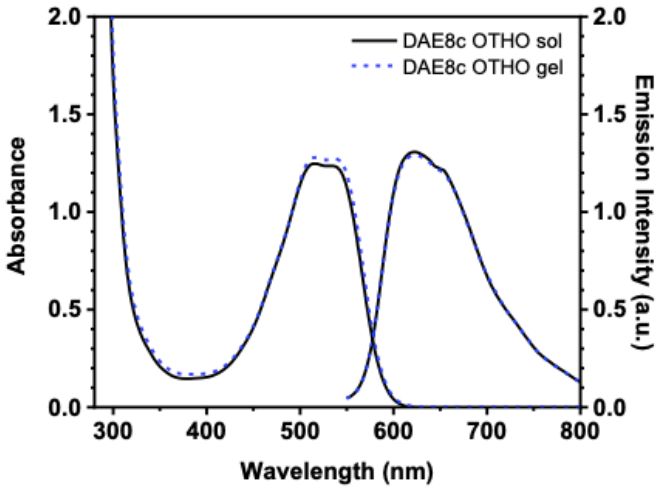
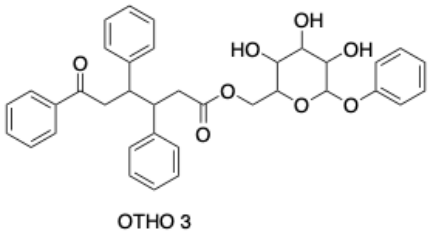


Figure S4. UV-Vis absorption and emission spectra of DAE8 (10^{-5} M) in toluene. λ_{ex} = 420 nm.

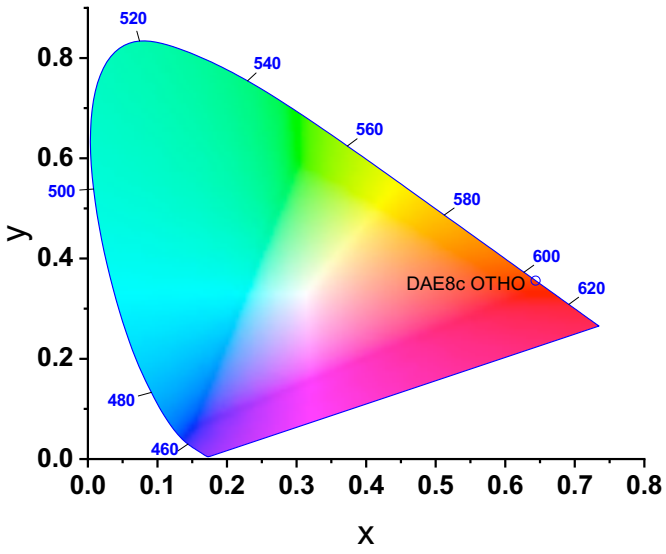




OTHO 3

Figure S5. UV-Vis absorption and emission spectra of DAE8c in the presence of unfunctionalized OTHO3 as solution and gel state in toluene. λ_{ex} = 420 nm. No significant spectral changes were apparent, with only minor intensity differences observed due to a small amount of scattering in the gel sample. The formation of DAE8c is quantitative both in the sol and the gel state upon UV irradiation, due to the very inefficient photoisomerization from DAE8c to DAE8o (Uno *et al.*, *J. Am. Chem. Soc.*, **2011**, *133*, 13558-13564). This is also apparent from the absorption spectra, where no spectral features of DAE8o are seen between 320 nm and 400 nm (c.f. Figure S4 red line) after UV irradiation.

A)



B)

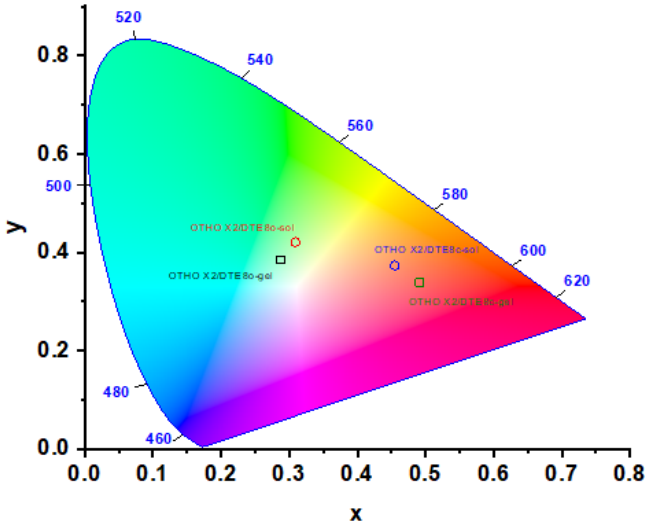


Figure S6. A) Overlapping CIE coordinates of DAE8c in OTHO3 (emission spectra unchanged in solution and gel). B) CIE coordinates of OTHO5/DAE8 with different combinations of the input triggers. The concentration of OTHO5 is 10 mg/mL, DAE8 is 10^{-3} M, toluene/acetonitrile = 2:1. The spectra were recorded at room temperature with λ_{ex} = 370 nm. This increase in the concentration of DAE8 results in a shift of the CIE coordinates to higher x-values as compared to when the concentration of the DAE8 is 10^{-4} M (figure **4B)**. The molar ratio that gave the largest separation of the coordinates in the CIE diagram ([DAE8] = 10^{-4} M) and thus, also the largest color differences, was chosen for this study.

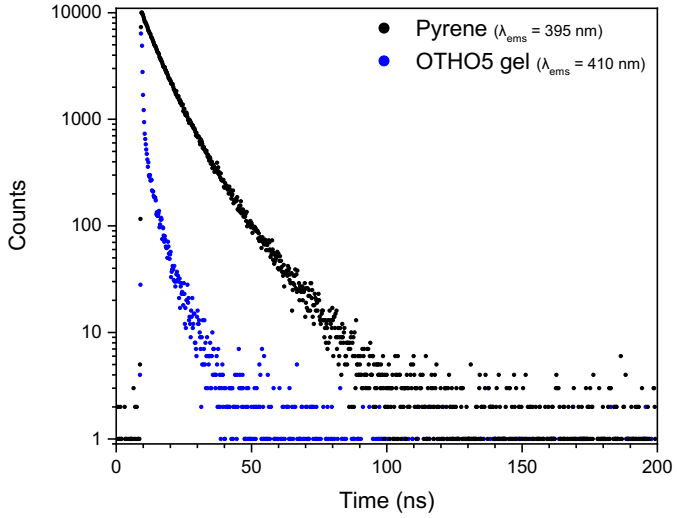


Figure S7. Time-resolved emission decays of pyrene (1.4 x 10^{-2} M) and **OTHO5**-Gel (10 mg/mL) in toluene. λ_{ex} = 377 nm, λ_{ems} = 395 nm and 410 nm for pyrene solution and gel, respectively.

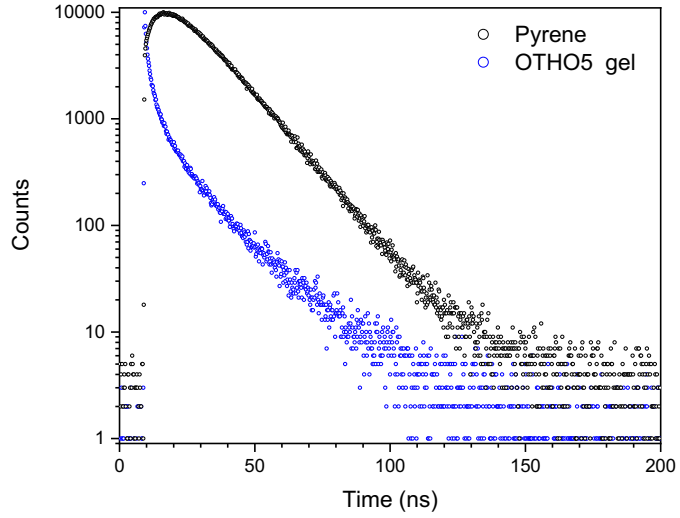


Figure S8. Time-resolved emission decays of pyrene (1.4 x 10^{-2} M) and **OTHO5** gel (10 mg/mL) in toluene. λ_{ex} = 377 nm, λ_{ems} = 500 nm.

Table S2. Fluorescence lifetimes of pyrene solution (1.4 x 10^{-2} M) and **OTHO5** gel (10 mg/mL) in toluene.

Sample	λ_{ems} [nm]	Lifetime [ns]			Pre-exponential factors			
		τ_1	τ_2	τ_3	α_1	α_2	α_3	χ^2
Pyrene solution	395	5.1	10.6	-	0.55	0.45	-	1.00
	500	6.5	14.2	-	−0.46	0.54	-	1.09
OTHO5 gel	410	0.5	4.0	-	0.58	0.42	-	1.21
	500	0.5	3.5	16.5	0.61	0.31	0.08	1.16

Calculation of spectral overlap integral

Software: a|e - UV-Vis-IR Spectral Software 2.2, FluorTools, www.fluortools.com

Molar absorption coefficient of DAE8c = 6.2 × 10^4 M^{-1} cm^{-1} at 506 nm, from K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.* **2011**, *133*, 13558-13564.

Approximation of pyrene fluorescence quantum yield: Φ_F = 0.32, from I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules (Second Edition)* (Ed.: I. B. Berlman), Academic Press, **1971**.

Spectral overlap integral (J) of DAE8c and **OTHO5** (solution) = 1.919 × 10^{15} M^{-1} cm^{-1} nm^4, R_0 = 42.0 Å

Spectral overlap integral (J) of DAE8c and **OTHO5** (gel) = 1.608 × 10^{15} M^{-1} cm^{-1} nm^4, R_0 = 40.7 Å

Average nearest neighbor distance between DAE8 ≈ 140 Å

R_0, (the donor-acceptor distance at which the FRET efficiency is 50%) is significantly shorter than the average nearest neighbor distance between DAE8 molecules. Thus, very few pyrene donor molecules are at distances smaller than R_0 from the nearest DAE8 acceptor, and FRET is not expected to make a significant contribution to the overall decay of the pyrene fluorophore. This notion is supported by time-resolved fluorescence measurements, in which the decays of pyrene show no significant change when mixed with DAE8 at 10^{-4} M (Figure S9).

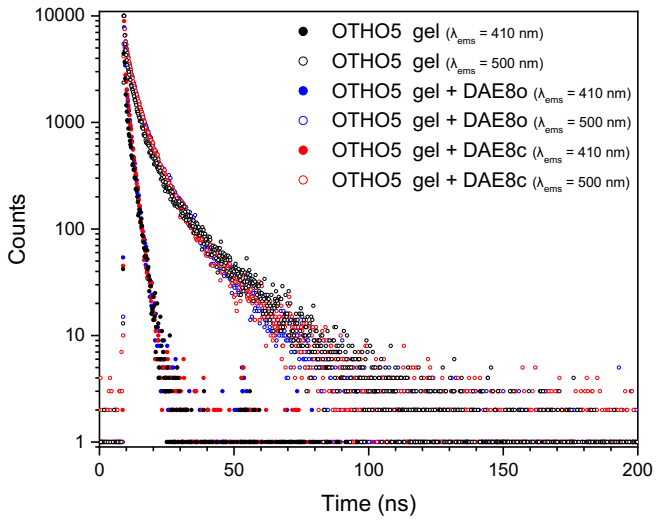
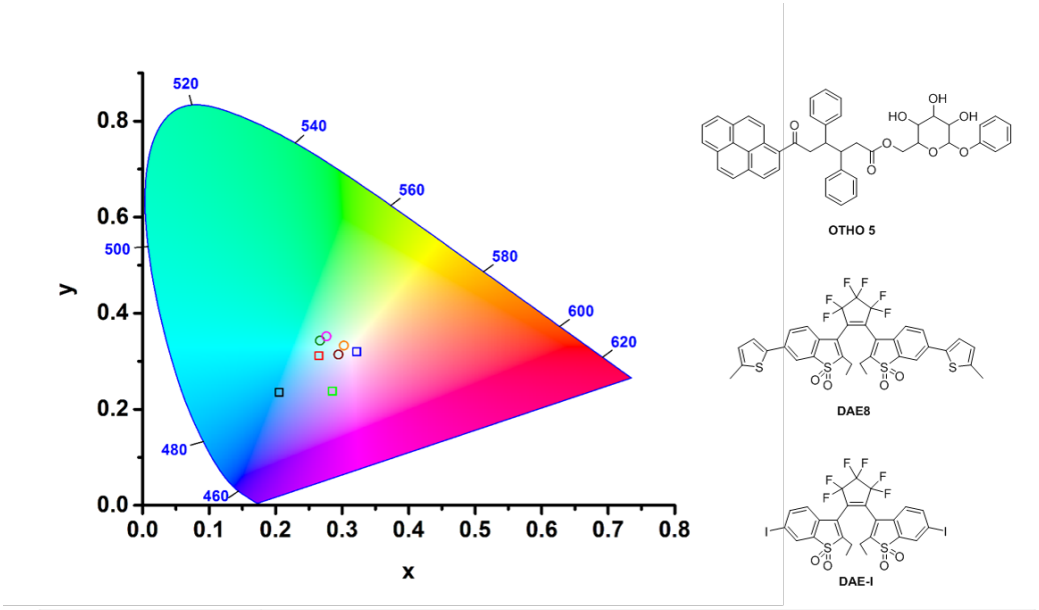


Figure S9. Time-resolved emission decays of **OTHO5** (10 mg/mL) with and without DAE8 (10^{-4} M). λ_{ex} = 377 nm, toluene/acetonitrile = 2/1.



Emission Readout CIE (x,y)		Input 2 & 3			
		Dark	300 nm	425 nm	300 + 425 nm
Input 1	Solution	0 (0.267, 0.343)	2 (0.276, 0.352)	4 (0.303, 0.333)	6 (0.295, 0.314)
	Gel	1 (0.206, 0.235)	3 (0.265, 0.311)	5 (0.286, 0.237)	7 (0.322, 0.319)

Figure S10. CIE coordinates of **OTHO5**/DTE8/DAE-I with different inputs. The concentration of **OTHO5** is 10 mg/mL, DAE8 is 10^{-4} M, DAE-I is 10^{-3} M, toluene/acetonitrile = 2/1. The spectra were recorded at room temperature with λ_{ex} = 370 nm. λ_{ex} = 425 nm was used for DAE8 isomerization and λ_{ex} = 300 nm was used for DAE-I isomerization.

G. NMR spectra

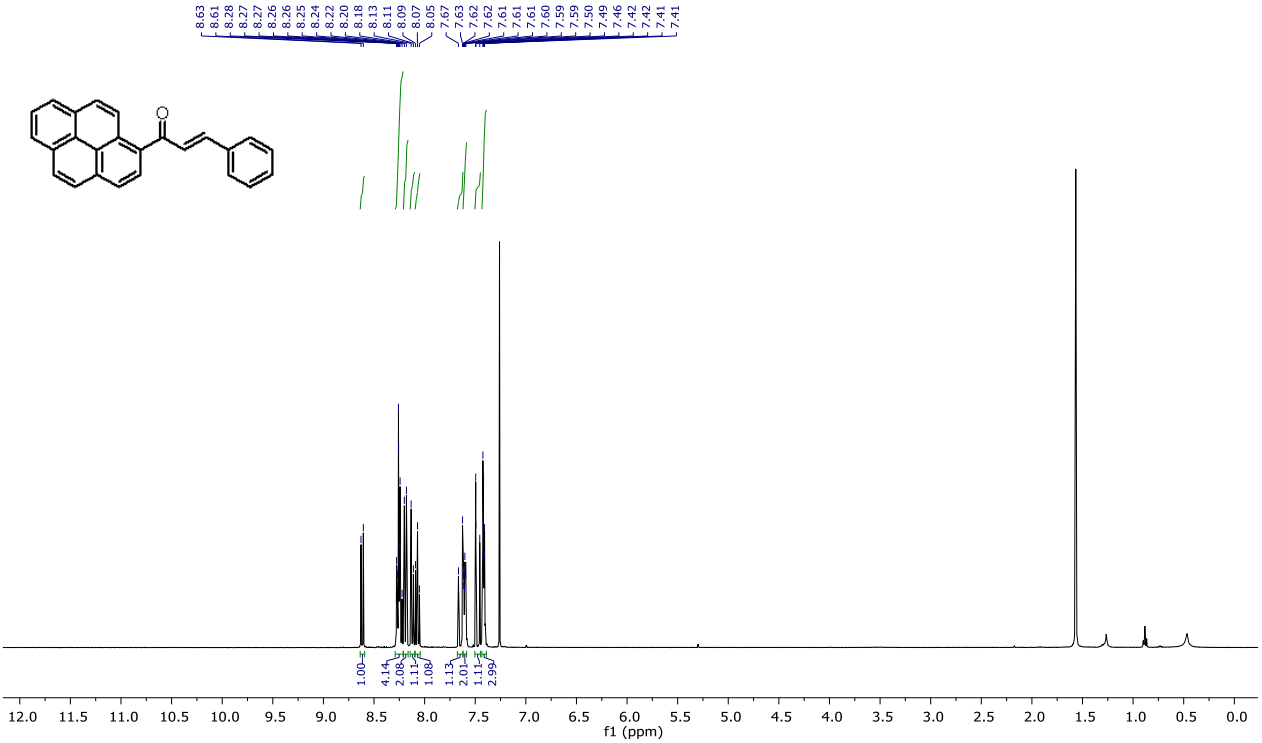


Figure S11. ^{1}H NMR spectrum of 1-pyrenyl-chalcone (**1**), 400 MHz, $CDCl_3$, 298 K.

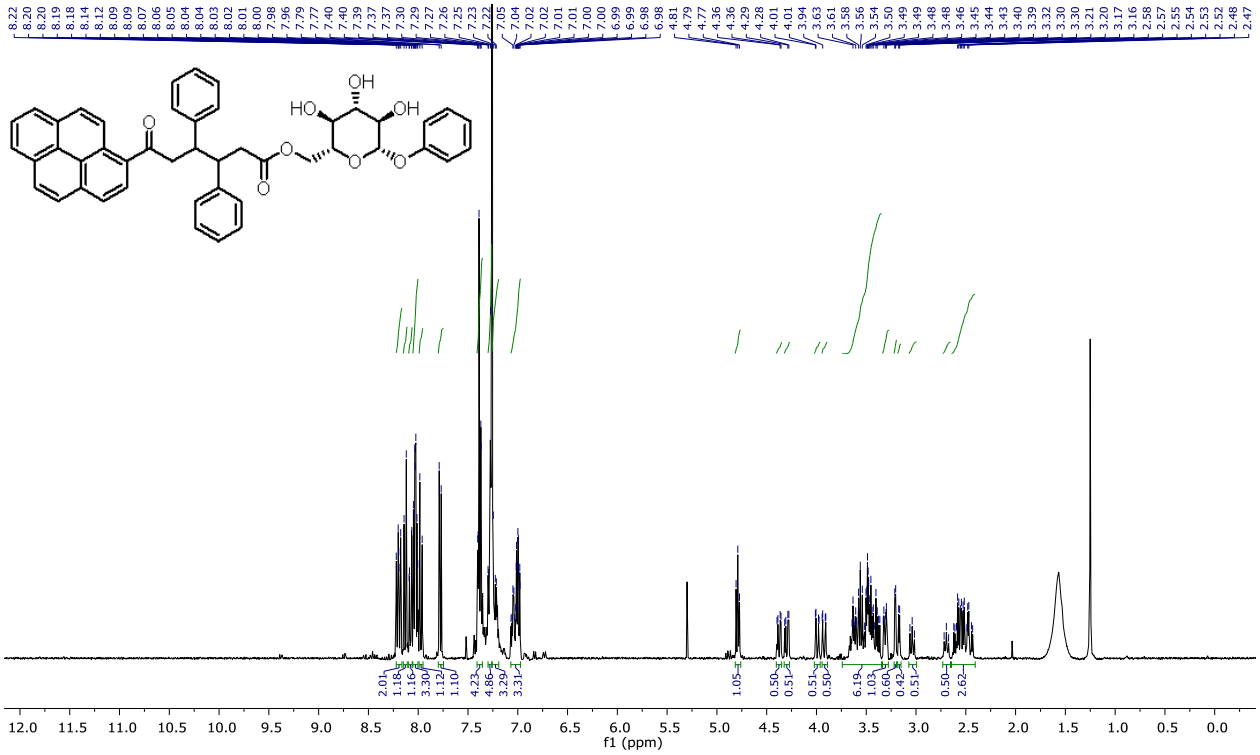


Figure S12. ^{1}H NMR spectrum of **OTHO5**, 400 MHz, $CDCl_3$, 298 K.

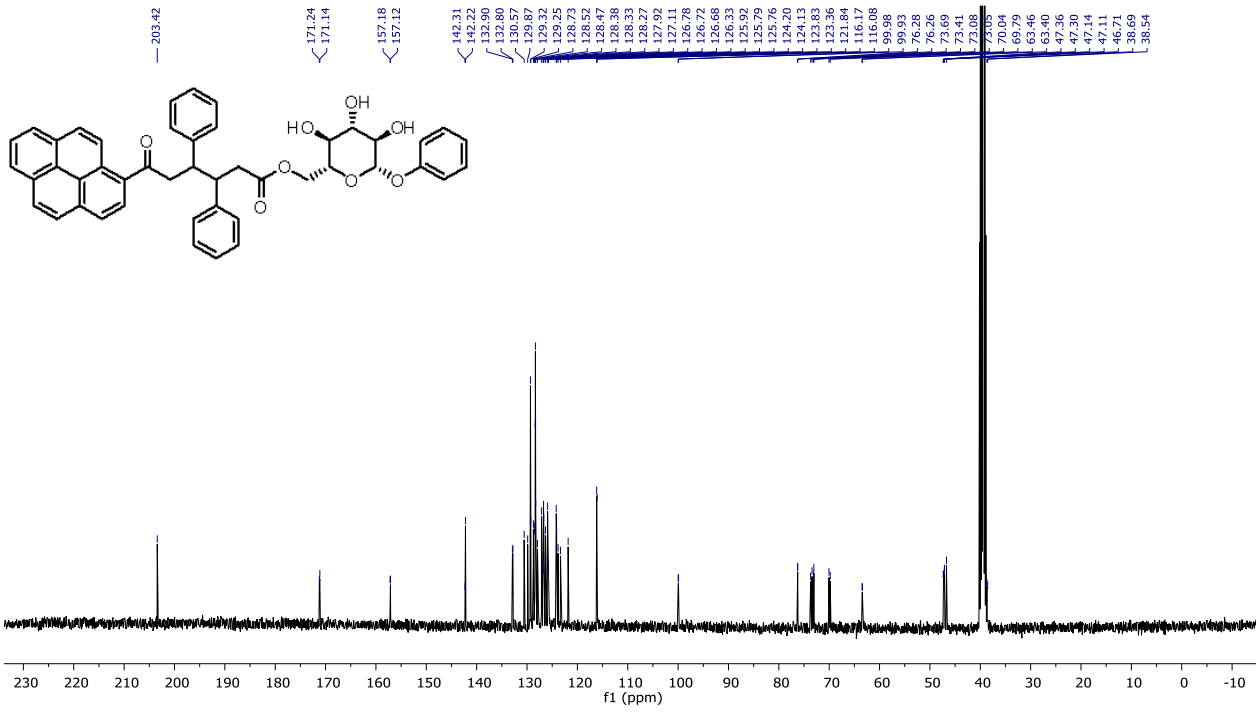


Figure S13. ^{13}C NMR spectrum of **OTHO5**, 400 MHz, DMSO-d_6, 298 K.